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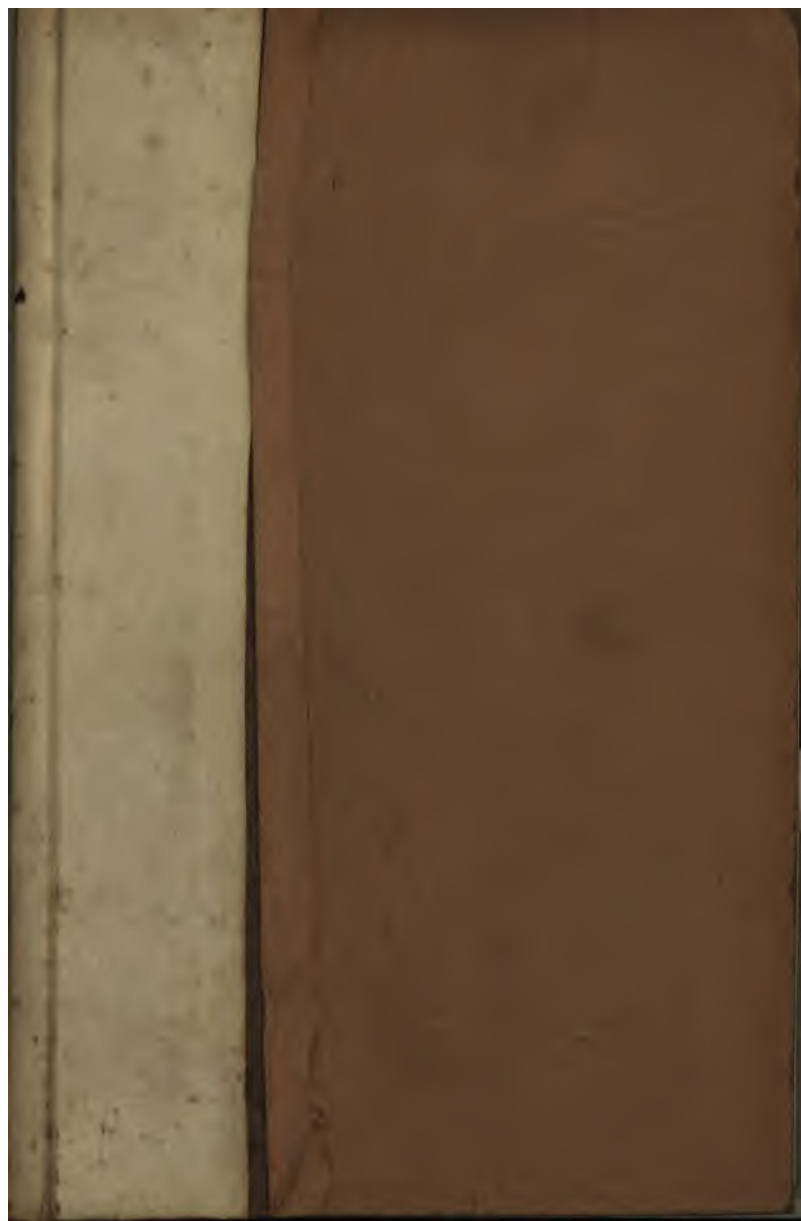
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ELEMENTARY TREATISE

ON

PHOTOGRAPHIC CHEMISTRY.

BY

ARNOLD SPILLER.

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PREFACE.

IN setting before myself the task of writing a short elementary treatise on Photographic Chemistry, I have been guided by the consideration that the practical photographer stands in need of a handy-book of references to aid him in the testing of the materials with which he ordinarily works, rather than having recourse to one of the more bulky treatises wherein the information he seeks is necessarily wrapped up with theoretical teaching and formulæ, which, for his purpose, often defeat the object in view.

The limited space at my disposal has further rendered necessary this mode of treating the subject; but I trust that the processes of analysis, set forth in the following pages, will supply all that is wanted in ordinary cases, and assist the student to test for himself the purity of photographic chemicals—prominence being given to the simplest methods, and to the modern systems of volumetrical analysis, by which time is saved and accurate results secured. Of course the student may, after this preliminary instruction, proceed to work out more difficult problems, being then guided by one of the recognized manuals treating at greater length of the general processes of chemical analysis. A. S.

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CHAPTER I:

APPARATUS.*

IN dealing with this subject, we shall treat of it under three headings: Firstly, "apparatus required for the simple testing of photographic chemicals"; secondly, "apparatus required for the preparation of certain photographic chemicals"; and thirdly, "apparatus necessary for the estimation of photographic chemicals." In this way the student can take up any one of the three branches without buying apparatus which may be useless to him. For the first-named purpose, the following apparatus will be required :—

Test-tubes and stand.

Tube-cleaner.

Spirit lamp or Bunsen gas-burner, with rose top.

Retort stand.

Wash bottle.

Small evaporating-basin.

Funnel.

* The woodcuts are of apparatus supplied by Messrs. J. J. Griffin and Co., of Garrick Street, W.C.

Filter paper.

Platinum wire.

Sulphuretted hydrogen generator.

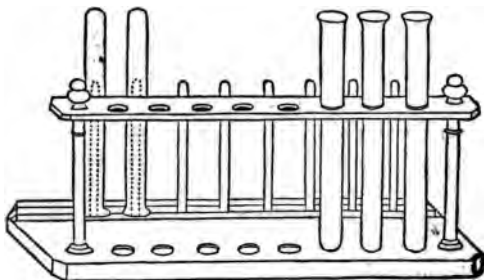
Two watch glasses.

Glass rod and tubing.

Triangular file.

Test-tubes are made of thin, hard glass tubing closed at one end, and should be about five inches long by three-quarters of an inch in diameter; they are used for dissolving the substance to be tested, and for experimenting upon it in a manner to be described in a future lesson.

Test-tube stand, as the name implies, is used for holding test-tubes in a convenient position.



Test Tube Stand.

Tube cleaner consists of a piece of wire with bristles worked in at one end. To use it, soak the bristles in water and push into the test-tube, when any dirt adhering to the inside will be quickly removed.

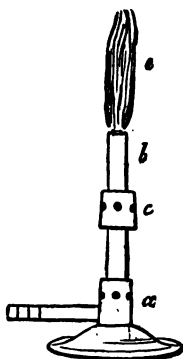
Spirit lamp is a glass bottle with a perforated brass cap through which an ordinary wick passes. Methylated spirit is placed in the bottle, and a ground glass cap is used to

extinguish the flame and prevent the evaporation of the spirit when not in use.

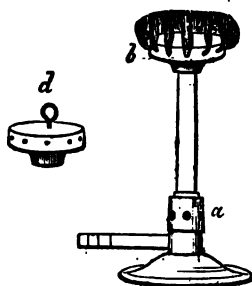


Spirit Lamp

Bunsen burner should be used in preference to a spirit lamp where gas is laid on. The burner consists of an upright brass tube about three inches high, through which the gas passes; at the bottom are situated two holes for the inlet of air. On applying a light at the top of the tube



Bunsen Burner.

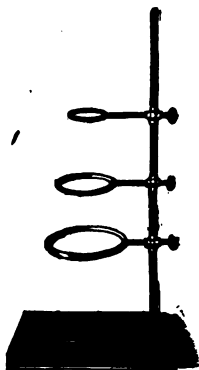


Burner with Rose.

the gas burns with a colourless flame, which is incapable of smoking anything placed in it. A brass cap perforated

with six or eight holes, called a "rose," is placed on the top of the burner to diffuse the flame when a gentle heat is required.

Retort stand is simply a vertical iron rod fitted with two.

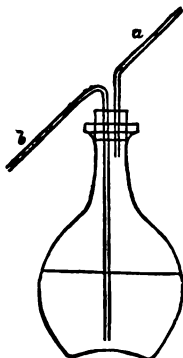


Retort Stand.

or three rings, which can be adjusted to any convenient height above the stand. It is used for holding evaporating basins, beakers, and flasks whilst being heated, or for supporting a funnel during filtration.

Wash bottle may be used as a convenient vessel for distilled water; but its chief use is for washing precipitates on filters. This apparatus may be constructed of any bottle at hand; or, where it is desired to boil the water, a flask should be used. To the bottle is fitted an ordinary cork perforated with two holes, through which two bent glass tubes pass, one of which should reach to the bottom of the bottle, with the outer end terminating in a fine jet. The other tube need only be long enough to pass through the cork, and here the mouth is applied to blow the water

out of the bottle up the long tube through the jet in a fine stream on to the filter.



Wash Bottle.

Evaporating basin is a shallow vessel made of thin porcelain, and for analytical purposes should be about three inches in diameter. In order to evaporate a solution, pour it into the basin supported on a ring of the retort stand; now place a spirit lamp or gas burner fitted with a rose under the apparatus, and the heat applied will soon warm the water and drive it off in the form of steam, leaving the solid residue behind.

A small *funnel* about three inches in diameter is required for filtering any liquid containing a precipitate; the apparatus requires no further description, and no photographic laboratory is complete without one.

A packet of one hundred *filter papers*, about four inches in diameter, will be required for use with the funnel.

A piece of *platinum wire* four inches long, and about the

average thickness of a pin, is useful for the "colour-flame" test.

Sulphuretted hydrogen generator can be constructed of an ordinary six-ounce medicine phial by making a hole in the cork and placing it in a glass tube bent twice at right angles; one end need only be sufficiently long to go just through the cork, the other end should be about three inches in length. About an ounce of iron sulphide is placed in the phial, and, when the apparatus is required for use, about half an ounce of strong hydrochloric acid mixed with an equal volume of water is poured into it, and the tube and cork quickly placed in position, when a plentiful supply of the gas will escape from the tube. This operation should only be performed out of doors on account of the bad smell.

Watch glass is useful for holding solutions which necessitate stirring in order to prove the presence of such substances as potassium or sodium salts.

Two or three feet of *glass tubing* about three-sixteenths of an inch in diameter is required for making the wash bottle and sulphuretted hydrogen apparatus. To bend the tubing it must be placed in the upper part of the flame of an ordinary fish-tail gas burner till it is soft; it can then be bent to any required angle or drawn out to a jet; glass tube can be easily cut by scratching with a file and then breaking it.

In the second branch the following apparatus will be required:—

Four beakers,

Two flasks.

Dial glass.

Funnel.

Filter paper (a quire).

Bunsen burner.

Retort stand.

Glass rod.

Wire gauze.

Beakers are tumbler-shaped vessels made of very thin, hard glass, and will consequently hold boiling solutions without cracking; four will be required, holding, say, 20 ounces, 10 ounces, 4 ounces, and 2 ounces respectively.

Flasks are also made of thin, hard glass, and in appearance are not unlike decanters; those containing from ten to twenty ounces are of most useful size for ordinary purposes.

Dial glass, which is simply a large watch glass, is useful for covering a beaker to prevent evaporation, and keep out dust.

A ribbed or fluted *funnel* of about five inches in diameter is best for quick filtering.

Thick *filter paper* (bibulous) will be necessary for drying any moist solids or precipitates. A square or round piece, cut of convenient size, folded in four, and opened upon a funnel, constitutes an ordinary filter.

A few *glass rods* from eight inches to a foot long are useful for stirring solutions to facilitate dissolution.

A piece of coarse *wire gauze* about four inches square is necessary to stand beakers or flasks upon to equalise the temperature when being heated.

For the third branch of our subject the following apparatus will be required:—

Burette.

Burette stand.

Pipette.

Flask.

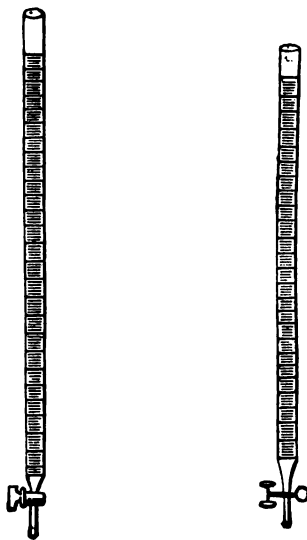
Evaporating basin.

Balance.

Weights.

Litre flask.

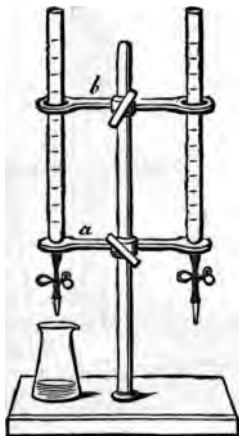
Burette is a long glass tube graduated into tenths of a



Burette.

cubic centimeter, and fitted with a stopcock at the bottom, consisting of either a metal clip pinching a small piece of india-rubber tube, or a glass stopcock. We show the two kinds of burette here, but should advise the student to use the one having a glass stopcock.

Burette stand is a necessary piece of apparatus for supporting the graduated tubes in upright position.

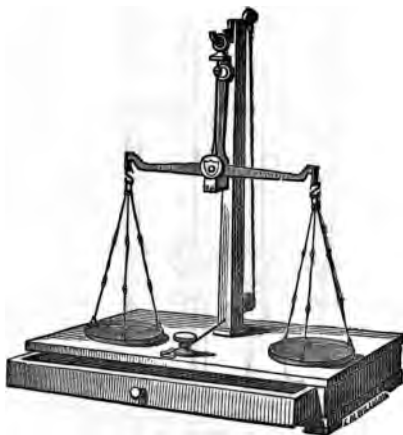


Burette Stand.

Pipette is a glass tube graduated into cubic centimetres, and drawn to a fine jet at both ends. It is used for delivering exact measures of standard solutions, which may easily be accomplished by inserting the lower end in the solution and applying suction at the top till the liquid has risen to the required point ; now place the finger on the top instead of the tongue, and in this way the pipette and its contents may be carried to any convenient vessel, and the measured liquid delivered into it.

A chemical balance is very expensive ; but one which answers all the requirements of the photographic student can be made with a good apothecary's balance (costing

about seven or eight shillings at Messrs. Griffins' establishment) fitted on a stand.



Scales on Stand.

A set of weights varying from ten to one hundredth of a gramme is indispensable, and should cost about seven-and-sixpence.

CHAPTER II.

REAGENTS.

In the quantitative analysis of photographic chemicals, the following solutions will be required :—

Solutions in 6-ounce Stoppered Bottles.

Sulphuric acid (strong).

„ „ (dilute).

Hydrochloric „ (strong).

„ „ (dilute).

Nitric „ (strong).

„ „ (dilute).

Acetic acid.

Potash.

Ammonia.

Ammonium sulphide.

Solutions in 2-ounce Corked Bottles.

Ammonium carbonate.

Ammonium chloride.

Ammonium oxalate.

Potassium antimoniate.

Potassium chromate.

Potassium iodide.
 Silver nitrate.
 Iron protosulphate.
 Lead acetate.
 Barium nitrate.
 Sodium phosphate.
 Tin protochloride.
 Platinum perchloride.
 Lime water.
 Starch solution.

Each bottle should be labelled with the name of the reagent and its symbol ; in that way it will greatly assist the student in learning the symbols of the various chemicals, and also save a great deal of time in taking notes of experiments. Labels can be had from philosophical instrument makers suitable for the purpose, but for those who prefer to make their own we append an example.

SULPHURIC ACID

(Strong)



Sulphuric acid, H_2SO_4 .—About eight ounces will be required. The dilute solution should contain about one of acid to three of water, but in making it up the water must be placed in a beaker, and the acid added slowly, stirring the whole time ; when cold, pour the mixture into a stoppered bottle.

Hydrochloric acid, HCl .—Eight ounces will be sufficient ; the dilute solution may be made by mixing three parts of water to one of acid, no precaution being necessary in mixing as in the former solution.

Nitric acid, HNO_3 .—Two solutions will also be required.

The dilute solution is made up after the manner of the hydrochloric acid solution.

Ammonia, NH_3 , otherwise known as *liquor ammonia*, when mixed with an equal volume of water, is of convenient strength.

Potash, KHO , better known as *caustic potash*.—About an ounce of the solid *stick* should be dissolved in six ounces of water.

Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$.—The strong acid should be mixed with about two volumes of water.

Ammonium sulphide, NH_4HS , is obtained by passing sulphuretted hydrogen through a solution of ammonia till it is saturated; the solution should be colourless, or only of a slight yellow colour. Sulphide of ammonium is a test for iron, forming with it a black precipitate of iron sulphide.

Ammonia carbonate $(\text{NH}_4)_2\text{CO}_3$.—A quarter of an ounce of the salt should be dissolved in two ounces of water; it is chiefly used as a precipitant of the alkaline earths.

Ammonium chloride, NH_4Cl , commonly known as *sal ammoniac*.—A saturated solution should be made up.

Ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$.—One drachm dissolved in two ounces of water will be required; it produces with calcium salts a white precipitate soluble in hydrochloric acid.

Potassium antimoniate, KSbO_3 .—One drachm must be briskly shaken with two ounces of water, and the solution filtered. It gives, with alkaline solutions of sodium salts, a granular precipitate on stirring.

Potassium chromate, K_2CrO_4 , is a yellow salt, and should be neutral, or only slightly alkaline; five grains dissolved in two ounces of water is of convenient strength. It is used as an indicator for the volumetric determination of silver,

and also as a test for salts of silver, forming a blood-red precipitate of silver chromate. When the solution of potassium chromate is kept in a glass bottle for some time, a yellow deposit of lead chromate is formed on the inside, by the combination of chromic acid with the lead in the glass.

Potassium iodide, KI.—Twenty or thirty grains dissolved in two ounces of water is a useful solution. It is a test for silver, mercury, and lead, giving pale yellow, scarlet, and bright yellow precipitates respectively. The scarlet mercuric iodide is readily soluble in an excess of potassium iodide. The lead iodide is dissolved by boiling water, but crystallizes out in beautiful golden spangles on cooling.

Silver nitrate, AgNO_3 .—Five grains dissolved in two ounces of water is sufficient. It is a test for chlorides, giving a white precipitate, soluble in ammonia; with bromides, it gives a cream-coloured deposit, only slightly soluble in ammonia; while with iodides, a yellow precipitate, totally insoluble in ammonia, is formed. Hypo-sulphite of soda forms with silver nitrate a white precipitate, which soon changes to the black sulphide of silver.

Iron protosulphate (ferrous sulphate), FeSO_4 .—Ten grains dissolved in an ounce of water is sufficient; but it will not keep longer than a month, from the fact that it absorbs oxygen from the air, and is converted into the ferric salt. If strong sulphuric acid is added slowly to a mixture of any nitrate and ferrous sulphate, a brown band is formed at the junction of the two liquids.

Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.—Twenty grains should be dissolved in two ounces of water. This solution is a test for sulphides, forming a black precipitate of lead sulphide.

Barium nitrate, $\text{Ba}(\text{NO}_3)_2$.—A solution containing half an

ounce dissolved in two ounces of water should be made. Its chief use is as a test for sulphates, forming a white precipitate insoluble in nitric acid.

Sodium phosphate (hydrodisodic phosphate), NaHPO_4 .—Half an ounce should be dissolved in two ounces of water. It is used as a test for magnesium compounds, with which it forms a white granular precipitate in the presence of ammonia.

Lime water, CaO .—A piece of quicklime about the size of a marble should be powdered up and shaken with two ounces of water, and then allowed to settle. The clear liquid must be decanted off. Lime water is used as a test for carbonates. The substance to be tested is placed in a test-tube fitted with a perforated cork holding a tube bent twice at right angles, the outer end dipping into another test-tube containing the lime water. Hydrochloric acid is poured on the substance, when a white deposit formed in the lime water will indicate the presence of carbonates.

Tin proto-chloride (stannous chloride), SnCl_2 , is prepared by boiling about twenty grains of metallic tin with two drachms of strong hydrochloric acid, and then diluting to two ounces of water. The solution will keep fairly well if a small piece of metallic tin is left in the solution. It gives with solutions of gold a purple precipitate, and with platinum a bright red solution.

Platinum perchloride (platinic chloride), PtCl_4 .—A solution containing ten grains in an ounce of water will be required. It produces with ammonium and potassium salts a crystalline precipitate when stirred.

Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$.—About ten grains should be dissolved in an ounce of water. This solution is used for distinguishing salts of iron; with persalts it

forms a dark Prussian blue precipitate, while with the proto-salts it gives a pale blue precipitate.

A packet of litmus paper (purple) is required for testing acids and alkalies; a red colour is formed by acids, and a blue by alkalies. About a gallon of pure distilled water is required for making up the above solutions, and also the standard solutions, &c., required in quantitative estimations. Stills are sold on purpose for purifying water, but it is far better to buy distilled water from the druggist, taking care to test for chlorides before using it. Of course everyone knows that in testing for chlorides all that is necessary is to add a few drops of silver nitrate to the suspected water, which, if it be impure, will form a white milky cloud. Filtered rain-water is the best substitute for the above.

CHAPTER III.

PHOTOGRAPHIC CHEMICALS.

Acetic acid, $C_2H_4O_2$, is the essential constituent of vinegar; the liquid known as *glacial* acetic acid contains 99 per cent. of the real acid, and is obtained by distilling sodium acetate and sulphuric acid. It may be recognised by its odour of vinegar, and also by heating with alcohol and sulphuric acid, when the characteristic odour of acetic ether will be produced.

Citric acid, $C_6H_8O_7$, is obtained from fermented lemon juice. The latter is neutralised with chalk, and the insoluble calcium citrate is decomposed with sulphuric acid, the sulphate of calcium is filtered off, and the citric acid crystallised out after evaporation. The acid is very soluble in water and alcohol, and when heated with strong sulphuric acid it gradually blackens, with evolution of carbonic oxide, which burns with a blue flame.

Gallic acid, $C_7H_6O_5$, is prepared by boiling powdered nutgalls with extremely dilute sulphuric acid, and then allowed to cool, when the gallo-tannic acid in the galls is decomposed into grape sugar and gallic acid, which crystallizes out in yellow needles. Gallic acid is sparingly

soluble in cold water, although readily soluble in hot water. When added to a solution of perchloride of iron it produces an inky-black precipitate, and with ammonia it forms a red brown solution which darkens when shaken in the air.

Pyrogallie acid, $C_6H_6O_3$, is manufactured on the large scale by heating gallic to about $200^\circ C.$ ($392^\circ F.$), by which means it is split up into carbonic anhydride and pyrogallie acid. It is very soluble in water, alcohol, and glycerine, and may be distinguished from gallic acid by its property of producing a dark brown colour when an alkaline solution is shaken in contact with air. Pyrogallie acid is not, strictly speaking, an acid, and its solution will not redden litmus paper; thus it is termed by chemists *pyrogallol*.

Hydrochloric acid, HCl , is an aqueous solution of the gas formed in the preparation of sulphate of soda from common salt and sulphuric acid. The acid is recognized by its property of reddening litmus paper, forming a white precipitate with silver nitrate, and its pungent odour.

Nitric acid, HNO_3 , is prepared by distilling a mixture of potassium nitrate and sulphuric acid. Strong nitric acid has a specific gravity of 1.42; while the acid known as "fuming nitric" should have a specific gravity of 1.52, and often possesses a yellow colour, from the presence of nitric peroxide. The acid may be detected by its property of producing red fumes when heated with metallic copper, and a brown colouration with a solution of ferrous sulphate.

Sulphuric acid, H_2SO_4 , is produced by the oxidation of sulphurous anhydride; on the large scale it is manufactured by allowing sulphurous anhydride, steam, air, and nitrous fumes to mix in a series of leaden chambers, where they all react to form the acid, which collects at the

bottom of the chambers. The acid in this condition is somewhat dilute, so in order to concentrate it the acid is placed in a platinum still and distilled till it is of the specific gravity 1.82, when it is in the condition known as "commercial acid" or "oil of vitriol." It generally has a brown colour, from the presence of organic matter, and it also contains an appreciable amount of lead. Pure sulphuric acid is obtained by distilling the commercial acid, thus freeing it from lead, organic matter, &c. The acid may be identified by its property of blackening sugar, and producing a white precipitate with a solution of a barium salt.

Alcohol is, correctly speaking, the name of a series of organic compounds; but that which is generally understood by "alcohol" is ethyl alcohol, C_2H_5O , or C_2H_5HO , or spirits of wine, and is obtained by the fermentation of sugar in presence of yeast.

Methylated spirit is a mixture of three parts of ethyl alcohol and one of methyl-alcohol—a liquid obtained by the distillation of wood. The object of adding the methyl-alcohol is to prevent the use of the spirit for manufacturing intoxicating liquors.

Spirits of wine should be of specific gravity .825, containing 10 per cent. of water; while absolute alcohol (which is prepared by distilling the above with quicklime) is of specific gravity .794, and should not contain a trace of water. Ethyl alcohol may be recognised by its property of producing the characteristic odour of acetic acid when heated with a mixture of sulphuric acid and potassium bichromate.

Alum, $AlK(SO_4)_2 \cdot 12H_2O$, or $AlNH_4(SO_4)_2 \cdot 12H_2O$, is a double sulphate of either potassium or ammonium and aluminium; the alums are made by adding a solution of

aluminium sulphate—prepared from clay and sulphuric acid—to a solution of sulphate of the alkali. The potash alum is generally found in commerce, but ammonia alum is occasionally met with, and can be distinguished by its power of evolving ammonia when treated with a solution of caustic soda or potash. Both potash and ammonia alum produce a white precipitate with a solution of barium chloride, and a violet colour with a solution of logwood.

Chrome alum, $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, is obtained as a secondary product in the oxidation of substances by potassium bichromate and sulphuric acid, and is formed in the bichromate battery. This salt forms large dark purple crystals, which exhibit a ruby colour by reflected light. Chrome alum may be identified by its property of being oxidised when heated with nitric acid and potassium chlorate; the presence of chromic acid being afterwards proved by the addition of a solution of acetate of soda and lead acetate, when a yellow precipitate of lead chromate will be formed.

Ammonia liquor is a solution of ammonia gas (NH_3) in water, one volume of the liquid containing about six hundred volumes of the gas in solution. The ammonia is obtained by heating a mixture of ammonium chloride and lime, and the solution is formed by passing the gas thus formed into water. The liquid is generally known in commerce under the name of *liquor ammonia fort.*, and is of specific gravity .88, containing nearly 30 per cent. of ammonia. The only impurity that is likely to be present is the carbonate, which is formed by direct combination with the carbonic acid present in the atmosphere. Ammonia is recognised by its well-known pungent odour, and its property of bluing litmus.

Albumen is the principal constituent of white of egg

and the serum of blood. White of egg consists of cellules containing a solution of sodium albumenate, together with sodium chloride and calcium phosphate. In order to prepare pure albumen, the white of fresh eggs is briskly agitated with water, whereby the cellular compound separates out, and the sodium albumenate enters into solution. To remove the mineral substances a small quantity of basic lead acetate is added to the solution, producing a bulky precipitate of lead albumenate, which is thoroughly washed in water, and carbonic acid gas passed through the pasty mass. The carbonic acid decomposes the lead albumenate, forming lead carbonate, which separates as a precipitate, leaving the albumen in solution. In order to free it from the last traces of lead, a few drops of an aqueous solution of sulphuretted hydrogen are added, and the solution heated till the albumen begins to coagulate. It is then filtered, and evaporated at a temperature not exceeding 110° F.

When a solution of albumen is heated to 140° F. (60° C.), a white flocculent precipitate of an insoluble modification of albumen separates, the chemical composition of which is apparently the same.

Commercial albumen is simply dried white of egg, and consequently contains a considerable portion of mineral salts.

Ammonium bromide, NH_4Br , is produced when hydrobromic acid is neutralized with ammonia. The salt is very soluble in water, slightly deliquescent (*i.e.*, absorbs water), and gives off brown fumes of bromine when heated with strong sulphuric acid.

Ammonium chloride, NH_4Cl , commonly known as *salt ammoniac*, is manufactured by neutralizing the ammoniacal liquor obtained from the gas works with hydrochloric

acid, and, after evaporating the liquid, the residue is heated to sublimation, and the salt condensed, in iron domes, in the form of a white, tough, crystalline mass. The chief impurity which is met with in commercial ammonium chloride is iron, for if a strong solution of the salt is allowed to stand, a brown flocculent precipitate of oxide of iron will be deposited on the bottom of the vessel.

Ammonium chloride forms a white precipitate with a solution of silver nitrate, and evolves ammonia when treated with caustic soda or potash.

Cadmium bromide, $\text{CdBr}_2 \cdot \text{H}_2\text{O}$, is prepared by dissolving cadmium oxide or carbonate in hydrobromic acid, or by attacking the metal cadmium with bromine water, and the salt crystallizes in white efflorescent (*i.e.*, gives off water) needles, which are very soluble in water and alcohol. Cadmium salts form with a solution of ammonia a white precipitate soluble in excess, and, with ammonium sulphide, a yellow precipitate, insoluble in excess.

Cadmium iodide, CdI_2 , is made in a similar way to the above salt, substituting hydriodic acid for the hydrobromic acid.

Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is prepared on the large scale by roasting sulphide of copper, and treating the mixture of cupric oxide and sulphate with dilute sulphuric acid, the crystalline product being obtained by evaporating the liquid. When copper sulphate is heated, it gives off its water of crystallization, and the blue crystals give way to a white powder. A solution of copper sulphate forms with ammonia a white precipitate of cupric hydrate which re-dissolves, on adding excess, to a brilliant blue liquid; if ferrocyanide of potassium be added, a chocolate brown precipitate will be produced.

Ether, $\text{C}_4\text{H}_{10}\text{O}$, is prepared by distilling a mixture of

alcohol and sulphuric acid, when the latter, having such a strong attraction for water, subtracts it from the alcohol, and thus leaving the compound known as ether. On the large scale, ether is prepared by heating a mixture of equal quantities of alcohol and strong sulphuric, and then gradually adding thirty parts of alcohol, and distilling, when the ether will condense, together with traces of alcohol and sulphurous acid. The crude product is mixed with a weak solution of potassium carbonate, which dissolves the alcohol, and absorbs the sulphurous acid, leaving the ether, which is of lower specific gravity than water, to rise to the top. The upper liquid is drawn off, and distilled with quicklime, when absolutely pure ether distils over. This process is very dangerous, from the fact that a mixture of ether and air is explosive, and, when distilling, a certain amount is very apt to escape condensation. For greater safety the heat should be applied through a water bath.

Methylated ether is prepared in the above way, substituting methylated spirit for the alcohol. Pure ether is of specific gravity .74 at 0° C., and boils at 95° F. It dissolves oils and fats, and may be identified by its characteristic odour of collodion.

Gelatine is obtained from bones, hide, horn, hoof-cartilage, &c. On the Continent gelatine is made by digesting bones in dilute hydrochloric acid, whereby nearly the whole of the mineral matter, consisting of calcium phosphate and carbonate, is dissolved out; it is then washed in running water for some hours, and the cartilage, which consists for the most part of ossein, is boiled with water, converting it into gelatine. In England, gelatine is prepared from buffaloes' hides. The skins are first treated with water to wash them, dried, and

cut up; the pieces are then soaked in lime-water for some time, and afterwards thoroughly washed in running water, and then boiled in water, and allowed to stand, when the clear liquid is decanted off, and cooled down, the resulting jelly being finally dried on nets. Gelatine is very variable in composition, from the fact that it is a mixture of two substances—glutin and chondrin—in different proportions; and since glutin is more soluble than chondrin, the solubility of a given sample of gelatine will depend chiefly upon which of these two substances is in excess. Glutin produces a white precipitate with a solution of mercuric chloride, while chondrin behaves in a similar way with lead acetate.

Dry gelatine is a yellowish substance, elastic, vitreous, hard, and brittle. When a gelatinous solution is heated for a long time it loses its power of setting, and is gradually converted into meta-gelatine—a substance apparently having the same composition as gelatine.

Gold trichloride, AuCl_3 , is obtained by dissolving gold in a mixture of hydrochloric and nitric acids, and evaporating the solution to dryness. This compound forms yellow crystals, which are very deliquescent, and its solution is reduced by ferrous salts, many vegetable and animal substances, oxalate of potassium, &c., the gold being precipitated as a purple powder. Gold chloride is soluble in alcohol and ether, and its solution forms a purple or brown precipitate with stannous chloride.

Gum Arabic is a vegetable substance, which exudes from the *acacia*, growing in Arabia. It forms transparent globules, usually having a yellowish tint, which are very soluble in water, and when mixed with dilute hydrochloric acid and alcohol it deposits a flocculent precipitate of *arabin*. When a solution of gum is added to a salt of

zinc, copper, calcium, &c., a precipitate consisting of arabate of the metal is formed. This property is made use of in photo-lithography.

Iron perchloride, Fe_2Cl_6 , is produced by dissolving iron in a mixture of three parts hydrochloric and one of nitric acid, and evaporating the solution to dryness. The salt is very deliquescent, and dissolves in water and alcohol. Its solution forms a dark blue precipitate with ferrocyanide of potassium, and with silver nitrate a white precipitate of silver chloride.

Iron oxalate, FeC_2O_4 , otherwise known as ferrous oxalate, is precipitated when a solution of oxalic acid or potassium oxalate is added to ferrous sulphate. It forms a pale yellow powder which is almost insoluble in cold water, and only sparingly soluble in boiling water. Ferrous oxalate is readily soluble in a solution of potassium oxalate, with which it forms a double oxalate of potassium and iron, $\text{K}_2\text{Fe}(\text{C}_2\text{O}_4)_2$.

Iron protosulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is obtained by dissolving iron or ferrous sulphide in dilute sulphuric acid, but on the large scale it is prepared, simultaneously with alum, by decomposing aluminous schists containing iron pyrites. Pure ferrous sulphate can be obtained by adding its aqueous solution to a large bulk of alcohol, when the salt is precipitated in the form of a bluish white powder. When the green crystals of ferrous sulphate are kept for some time, they gradually become covered with a brown powder consisting of basic ferric sulphate. A solution of ferrous sulphate forms, with silver nitrate, a grey precipitate of metallic silver, and with potassium ferrocyanide a light blue precipitate.

Kaolin is a porcelain clay, consisting for the most part

of silicate of alumina. Its chief use is for decolourising the silver printing bath.

Mercury bichloride, HgCl_2 , commonly known as *corrosive sublimate*, may be obtained by dissolving mercury in hydrochloric acid mixed with a small amount of nitric acid. On the large scale it is prepared by heating a mixture of mercuric sulphate, sodium chloride, and a trace of manganese dioxide, and collecting the resulting sublimate. When a solution of mercuric chloride is shaken with a small quantity of mercury, a white precipitate, calomel, is formed, which blackens on the addition of ammonia. Washed over a photographic negative it has the property of converting the reduced metallic silver into a white double chloride of silver and mercury, which is insoluble in water.

Platinum dichloride, PtCl_2 , may be obtained by dissolving platinum in nitro-hydrochloric acid, and, after evaporating to dryness, the platinic chloride is gradually heated to 400°F. , when chlorine is given off, and the platinous salt remains as a brown residue. A simpler method of preparing the salt is to treat a solution of platinic chloride with sulphurous acid, when the platinous chloride will separate out in the form of a yellow crystalline mass. It is insoluble in water or nitric acid, but is readily soluble in a solution of potassium chloride, with which it forms a double salt, known as *chloro-platinite of potassium*, $\text{PtCl}_2 \cdot 2\text{KCl}$, which is the compound used in the platinotype process.

Potassium bichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is obtained by heating chrome-iron ore with chalk, and constantly stirring the mass. After about twelve hours the compound is mixed with water and filtered, sulphuric acid being added till the solution is distinctly acid; it is then agitated with chalk to

precipitate the sulphate of iron, and, after allowing the liquid to stand, potassium carbonate is thrown into it, and the bichromate of potassium is crystallized out. The salt forms orange-coloured crystals, which dissolve in about ten parts of cold water and in about five parts of boiling water. A solution of potassium bichromate produces a red-brown precipitate with silver nitrate, and the characteristic odour of aldehyde, when heated with alcohol and sulphuric acid.

Potassium bromide, KBr , is prepared by adding bromine to a solution of caustic potash; when a certain amount of bromate is simultaneously produced, the liquid is evaporated to dryness, and the residue heated to fusion; this converts the bromate into bromide, and the salt is finally purified by crystallization. The salt forms white cubical crystals which are very soluble in water, but only sparingly so in alcohol. The commercial salt generally contains iodide of potassium as an impurity; it may be detected by adding one drop of a very dilute solution of silver nitrate (one grain to the ounce) to about ten grains of the sample to be tested dissolved in half an ounce of water. If the ordinary cream-coloured precipitate of silver bromide is produced the salt is free from iodides; but should a bright yellow precipitate of silver iodide be formed, the above impurity is present.

Potassium cyanide, KCN , is prepared by igniting the ferrocyanide; in this way it is decomposed into carbide of iron, nitrogen, and potassium cyanide, the latter being purified by crystallizing either from an aqueous or alcoholic solution. Cyanide of potassium is very soluble in water, and slightly so in alcohol containing a small proportion of water; the salt is deliquescent, and is decomposed by the carbonic acid of the atmosphere in the presence of

moisture, thus accounting for its odour of hydrocyanic acid (prussic acid). Commercial potassium cyanide is very impure, containing a large quantity of potassium carbonate; both the pure and impure samples are very poisonous, from the presence of prussic acid, the best antidote being a mixture of protosulphate and perchloride of iron in solution.

Potassium ferrocyanide, $K_4Fe(CN)_6$, otherwise known as *yellow prussiate of potash*, is manufactured on the large scale by heating together animal matter—such as horn, dried blood, and leather—with iron filings, and potassium carbonate; the fused mass is then treated with water, and the potassium ferrocyanide crystallized by evaporation. With ferrous salts potassium ferrocyanide produces a pale blue precipitate; while with ferric salts a dark blue precipitate of Prussian blue is formed.

Potassium ferricyanide, $K_3Fe(CN)_6$, otherwise termed *red prussiate of potash*, is obtained by passing chlorine through a solution of potassium ferrocyanide, and purifying the salt by crystallization. Potassium ferricyanide forms beautiful red crystals which are converted by light into the yellow potassium ferrocyanide; the solution produces a dark blue precipitate with ferrous salts, and a brown colour with ferric salts.

Potassium iodide, KI , is prepared by adding iodine to a solution of caustic potash, and, after evaporating the solution, the residue is gently heated to decompose the iodate formed in connection with the iodide. Potassium iodide forms white cubical crystals, which are very soluble in water and alcohol; the solution produces a bright yellow precipitate with silver nitrate, and liberates iodine with the production of a brown colour when added to chlorine water. The only impurities that are likely to be present

are potassium iodate and carbonate ; the former will give a slight brown tint if hydrochloric acid is added to the solution, while the latter impurity produces an effervescence when the acid is added.

Potassium oxalate, $K_2C_2O_4 \cdot H_2O$, or *neutral oxalate of potash*, is obtained by neutralising a solution of potassium carbonate with oxalic acid. The salt is moderately soluble in water, and, when pure, it is neutral to test-papers ; but it generally exhibits a slightly alkaline reaction from the presence of potassium carbonate. A solution of potassium oxalate forms a white precipitate with chloride of calcium, which is soluble in hydrochloric acid.

Pyroxyline, $C_{18}H_{22}(NO_2)_8O_{15}$, or *nitro-cellulose*, is prepared in a similar manner to gun-cotton, but with the addition of a small quantity of water. Several kinds of soluble cotton are prepared to suit different requirements. One method is to make a mixture of three parts nitric acid, two parts water, and nine parts sulphuric acid ; the mixture is kept at a temperature of 140° F., and tufts of cotton-wool are placed in it for about five or ten minutes ; the cotton is then thoroughly washed for some hours in running water, and finally dried by exposure to the sun's heat. Pyroxyline, when pure, is perfectly soluble in a mixture of equal parts of alcohol and ether, forming the liquid known as colloidion ; the cotton is also soluble in methylic alcohol (wood spirit) ; but it should be totally insoluble in ethylic alcohol.

Silver bromide, $AgBr$, may be prepared either by acting upon silver with bromide, or by precipitating silver nitrate with a soluble bromide. The compound is a cream-coloured powder slightly soluble in ammonia, and when acted upon by iodine water it forms the bright yellow silver iodide, and liberates bromine. If absolutely dry

chlorine is passed over dry silver bromide, bromine is set free, and silver chloride is formed.

Silver chloride, AgCl , is prepared in a similar manner to silver bromide, substituting chlorine and a soluble chloride for bromine and a soluble bromide. Silver chloride forms a white powder, very soluble in ammonia, potassium cyanide, and sodium hyposulphite. When acted upon by moist iodide or bromine, silver chloride is converted into iodide or bromide of silver; but dry iodine or bromine has no action on dry silver chloride.

Silver iodide, AgI , may be obtained in a like manner to the two preceding compounds; it is a bright yellow substance, insoluble in water, but moderately soluble in sodium hyposulphite and potassium cyanide. Silver iodide is unacted upon by moist bromine or chlorine; but dry chlorine or bromine converts dry silver iodide into silver chloride or bromide. If a solution of silver nitrate be precipitated with a mixture of potassium, iodide, bromide, and chloride, silver iodide will be first formed, then the bromide, and finally the chloride.

Silver nitrate, AgNO_3 , is prepared by dissolving silver in nitric acid, and evaporating the solution to dryness. The salt is moderately soluble in water, and slightly so in alcohol. The solution produces a white precipitate with sodium chloride, which is soluble in ammonia, but re-precipitated on the addition of nitric acid.

Sodium chloride, NaCl , or *common salt*, is the principal salt in sea water, and also rock salt. It is—as, of course, every one knows—very soluble in water, but practically insoluble in alcohol. A saturated aqueous solution precipitates soap and several dyes when dissolved in water.

When sodium chloride is acted upon by strong sulphuric acid, hydrochloric acid gas is given off, and may be

recognized by its pungent odour and the white fumes produced when ammonia gas is mixed with it.

Sodium hyposulphite, $\text{Na}_2\text{S}_2\text{O}_3$ —or, more correctly speaking, *sodium thiosulphate*—is prepared by boiling sulphur in a solution of caustic soda, and then passing sulphurous acid into the liquid till it is decolourized. The crystals contain four molecules of water, and, when heated, the salt dissolves in its own water of crystallization. Sodium hyposulphite dissolves the silver haloids—i.e., bromine, chlorine, and iodine—forming silver hyposulphite and the haloid of sodium.

Tannin or tannic acid, $\text{C}_{27}\text{H}_{22}\text{O}_{17}$, is a vegetable product contained in the bark and other parts of several plants. Tannin is the astringent principle of gall-nuts, from which it may be extracted by water, as in the preparation of ink. Its chief use is for tanning leather, the gelatinous membrane forming an insoluble substance with the tannin.

Uranium nitrate, $\text{U}_2\text{N}_2\text{O}_8\text{H}_2\text{O}$, is produced by dissolving uranium or either of its oxides in nitric acid. The salt forms bright yellow crystals, which are extremely soluble in water and alcohol. The solution forms a brown precipitate with ferrocyanide of potassium. When acted upon by light, in the presence of organic matter, uranic nitrate is reduced to uranous oxide.

CHAPTER IV.

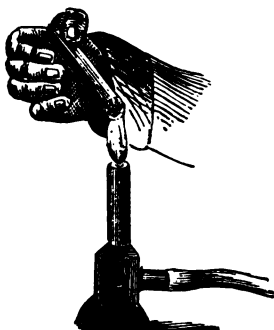
QUALITATIVE ANALYSIS OF CHEMICALS.

It may, perhaps, be asked by some, "What is the use of knowing how to analyse chemicals?—why not leave it to the analytical chemist?" This question we can answer in a very few words, for, in the first place, the photographic student will always take more interest in his work if he knows the chemical properties of the substances with which he works; and secondly, everyone knows how provoking it is to find, when searching for a chemical, that the label has come off the bottle, and it is doubtful what its contents may be; while, if only the photographer knows the rudiments of qualitative analysis, he will determine by a few experiments with the test-tube the value of the substance under consideration.

It must be remembered that the following description is only intended for the separation of chemicals that are likely to be met with in the photographic laboratory, and consequently the description and manipulation are much shorter and simpler than that necessary for the analysis of all chemicals apart from any photographic use.

About twenty grains of the substance should be placed

in a test-tube half filled with distilled water, and heat applied till the whole is dissolved (see fig.). The solu-



tion thus prepared is called the *original solution*. Pour about two drams of the solution into another test-tube, and add a few drops of hydrochloric acid. A white precipitate indicates the presence of *lead* or *silver*; add ammonia to the precipitate. If it dissolves, *silver* is present; but if unchanged, the substance is a compound of *lead*.

If no precipitate is formed with the hydrochloric acid, add to the *same* solution sulphuretted hydrogen water; a black precipitate indicates the presence of *copper*, *mercury*, or *gold*. To a fresh part of the original solution add ammonia. A yellow flocculent precipitate indicates *gold*, greenish blue dissolving in excess of ammonia to a cobalt blue solution proves the presence of *copper*, white dissolving in excess to a colourless liquid indicates *mercury*.

If no precipitate is formed with sulphuretted hydrogen, add to the original solution about a dram of ammonium chloride and a few drops of ammonia and sulphide of ammonium. A black precipitate indicates *iron*, white shows the presence of *aluminium*, and yellow indicates *cadmium*.

If no precipitate is produced in the previous instance, add to a fresh part of the original solution ammonium chloride, ammonia, and ammonium carbonate. A white precipitate indicates *calcium*.

If there is no reaction, add to the *same* solution sodium phosphate; a white precipitate forming slowly when stirred proves the presence of *magnesium*.

If no precipitate is produced, even on stirring, add to the original solution potash, and warm gently; the odour of ammonia proves the presence of a compound of *ammonium*.

If no odour is produced, place a few drops of a *strong* solution of the original substance in a watch-glass with one or two drops of hydrochloric acid and platinic chloride; stir with a glass rod. A yellow precipitate formed in lines on the surface of the watch-glass indicates *potassium*. Heat a little of the substance on a platinum wire in the flame of a spirit lamp or a Bunsen burner; a lilac-tinted flame confirms the presence of *potassium*.

If there is no reaction in either of the preceding experiments, repeat the watch-glass test, substituting potash and potassium antimoniate for the hydrochloric and platinic chloride. A white precipitate formed in lines proves the presence of *sodium*.

Having found the metal* or base, the next experiment is to determine what the acid is. Warm about ten grains of the substance with strong sulphuric acid in a test-tube.

Effervescence with inodorous gas indicates the presence of *carbonic acid*; confirm the experiment by passing the gas into lime-water (see Chapter II.).

Effervescence with pungent fumes, which form white

* Of course, in the case of gallic, pyrogallic, and citric acids, no metal is present[†].

clouds when brought near the stopper of the ammonia bottle, shows the presence of *hydrochloric acid*.

Yellow fumes which explode when heated strongly indicate *chloric acid*.

Brown fumes indicate *hydrobromic acid*, but slight brown fumes, which increase when metallic copper is placed in the liquid, indicate *nitric acid*.

Violet fumes prove the presence of *hydriodic acid*.

Yellow fumes of chlorine, which bleach moist litmus paper, indicate *hypochlorous acid* (the substance is probably chloride of lime).

Effervescence, with odour of burning sulphur, indicates *sulphurous acid*.

Odour of burning sulphur and yellow precipitate indicates *hyposulphurous acid*.

Effervescence with inflammable gas which burns with a blue flame indicates the probable presence of *oxalic acid*.

Gradual blackening, with evolution of inflammable gas, proves the probable presence of *citric acid*.

Odour of vinegar indicates *acetic acid*.

To confirm some of the preceding tests, dissolve about twenty grains of the substance in water ; to a small part of the solution add barium nitrate. A white precipitate, insoluble in nitric acid, indicates *sulphuric acid* ; yellow, soluble in nitric acid, indicates *chromic acid*.

To another part of the solution add silver nitrate. A white precipitate, insoluble in nitric acid, indicates *hydrochloric acid* ; yellow, insoluble in ammonia, proves the presence of *hydriodic acid* ; cream-coloured, slightly soluble in ammonia, indicates *hydrobromic acid*.

A white precipitate, insoluble in cold nitric acid, but soluble on boiling, indicates *hydrocyanic acid*.

A white precipitate, which blackens on standing, indicates *hyposulphurous acid*.

To a small part of the solution add sulphate of iron, and then gradually pour down the sides of the tube strong sulphuric acid. A brown ring at the junction of the two liquids indicates *nitric acid*; a light blue precipitate with sulphate of iron indicates *ferrocyanic acid*; a dark blue precipitate proves the presence of *ferricyanic acid*.

To another part of the original solution add acetic acid, acetate of ammonia, and calcium chloride. A white precipitate, soluble in hydrochloric acid, indicates *oxalic acid*.

To a fresh part of the solution add potash, and shake. A red colour indicates the presence of *gallio acid*; a brown colour, *pyrogallio acid*.

The student should first take known photographic chemicals, and go through the above series of tests, in which way he will accustom himself to the various reactions; after finishing that task he should get a friend to supply him with unknown chemicals, and in that way test his knowledge of analysis. Suppose, for instance, the student is given potassium chloride, after going through a series of experiments according to the above description, he obtains a precipitate with platinic chloride, which proves to him that the compound contains potassium; he next tests for the acid, and finds the substance produces pungent fumes when heated with sulphuric acid, and that the solution forms a white precipitate with silver nitrate, insoluble in nitric acid, which indicates that the compound also contains hydrochloric acid: the substance is therefore potassium chloride.

After having tested the substance, the student is advised to read the description of it in the preceding chapter on "Photographic Chemicals," so as to confirm his results by performing any extra tests that may be described therein.

CHAPTER V.

PREPARATION OF PYROGALLIC ACID, GALLIC ACID, AND HYDROKINONE.

THERE are several methods of preparing gallic acid, but the one which is simplest to carry out on the small scale is by heating an infusion of gall-nuts with a dilute solution of sulphuric acid. Take about a quarter of a pound of powdered gall-nuts, place it in a pint beaker, and pour about half a pint of boiling water into it, and allow the mixture to stand for an hour. Place over a large funnel a piece of calico about a foot square, and turn the contents of the beaker into the calico, but of course allowing the liquid which passes through the funnel to drop into a suitable vessel. When all has drained through, the calico is held by the corners, and thoroughly squeezed in order to press out the adherent liquid; this is then mixed with the liquid which drained through, and the whole is filtered through bibulous paper. Now pour the filtered solution into a pint flask, with half an ounce of dilute sulphuric acid (1:4), and boil over a sand-bath for a quarter of an hour; then let the solution cool down, when beautiful

needle-like crystals of gallic acid will separate out. The gallic acid thus prepared is somewhat impure, so to purify it, the crystals, after draining, are placed in a flask with about five ounces of water, and boiled till all is dissolved; the solution is filtered, while still hot, through bibulous paper, and the filtered liquid will deposit, on cooling, gallic acid which is moderately pure; the crystals are finally dried by pressing between two or three thicknesses of bibulous paper.

In preparing pyrogallic acid, one has the choice of several methods, viz., heating gallic acid alone, heating a mixture of gallic acid and powdered pumice-stone in an atmosphere of carbonic acid, and heating a solution of gallic acid in glycerine. The method which is most conveniently worked by the photographer is that of heating a solution of gallic acid in glycerine, but we give details of the other processes, so that the student may experiment with them.

In order to prepare pyrogallic acid by the first-named process, about half an ounce of gallic acid is placed in a large porcelain crucible, a piece of thin cardboard perforated with several small holes is tied over the top of the vessel, and a cone of stout paper is placed over it. The crucible is placed in a sand-bath heated by a Bunsen burner fitted with a rose. The temperature should be kept at about 180°C . or 185°C . for some hours, when the gallic will gradually decompose into carbonic dioxide, various secondary products and pyrogallic acid, the latter compound condensing in the paper cone. The great objection to this process is, that there is a great difficulty in maintaining the right temperature, for should it exceed 185°C ., the gallic acid is converted into meta-gallic acid and water; consequently, the above process does not yield

more than twenty per cent. of the original weight of the gallic acid.

The second method is a modification of the preceding process, and was proposed by Liebig. About half an ounce of gallic acid is mixed with one ounce of coarsely-powdered pumice, and placed in a six-ounce tubulated glass retort; the latter is placed on a sand-bath heated with a Bunsen burner to the same temperature as is necessary in the first method. In the tubulure of the retort is fitted a perforated cork, and a tube connected with a carbonic acid apparatus (the sulphuretted hydrogen generator containing lumps of white marble and hydrochloric acid will answer very well). The pyrogallic will gradually form on the inside of the neck of the retort, and can be easily removed by a glass rod. If the latter process be carried out correctly, about thirty per cent. of the original weight of gallic acid is formed. The reason why a greater yield is produced than in the former method is that the carbonic dioxide carries away the pyrogallic acid as soon as it is formed, and consequently prevents it being decomposed to a certain extent by a rise of temperature.

The next method is that of heating an aqueous solution of gallic in a sealed vessel to about 200° C.; after about half an hour the solution is boiled with animal charcoal, filtered, and evaporated to dryness, the residue being afterwards distilled under diminished pressure. In this process almost the theoretical yield is produced; but the process is not easily worked on the small scale, as a special apparatus is required for heating the solution of gallic acid and for distilling the impure pyrogallic acid under pressure. The process of heating a solution of gallic acid in glycerine has lately been suggested by Professor Thorpe, and is certainly the simplest and most economical method

for working on the small scale. Place in a four-ounce hard glass flask 300 grains of gallic acid and two ounces of Price's glycerine; fit in the neck of the flask a cork perforated with two holes, one being left open for the escape of gas, and through the other place a thermometer capable of registering 200° C. or 400° F., the bulb of which must dip into the liquid. Now heat the flask on a sand-bath to about 190° C. or 200° C. (400° F.), till the evolution of carbonic dioxide stops, which operation generally takes about an hour. The solution can now be preserved in a stoppered bottle for months without any apparent change. Each ounce of the liquid will contain about 100 grains of pyrogalllic acid, but Professor Thorpe prefers to pour the solution into 66 ounces of water, and in that way he obtains a solution which contains rather more than three grains to the ounce; the pyrogalllic acid in so dilute a solution will not keep more than a month.

Hydroquinone or hydrokinone, which substance has lately been proposed as a developing agent, may be prepared by distilling an extract of the cinchona bark or the coffee-berry with a mixture of sulphuric acid and manganic dioxide, and finally reducing the quinone thus obtained by dissolving it in water containing sulphurous acid, and evaporating the solution. A simpler and more economical process, which has been suggested by Nietzki, is that of oxidizing aniline by means of potassium bichromate and sulphuric acid.

For preparing it on a small scale, pour into a quart flask a pint and a half of water, and then gradually add five fluid ounces of sulphuric acid, and allow to stand till quite cool. When ready, place the flask in a basin of water with a few lumps of ice floating in it, and pour an ounce of aniline into the dilute acid; then very slowly add powdered

potassium bichromate till the dark green precipitate first formed is dissolved. From two to three ounces of the salt is required. When the operation is finished, place about ten ounces of methylated ether in a Winchester quart stoppered bottle, and then pour the contents of the flask into the bottle, replace the stopper, and briskly shake the vessel for ten or fifteen minutes, and allow to stand. When the two liquids have separated, draw the top ethereal solution off into an evaporating-basin by means of a syphon, and place the dish in the open air (if possible in the sun) for two or three hours, when the ether will evaporate, leaving crystals of quinone. While the evaporation of the ether is proceeding, a solution of sulphurous acid in water should be made. An apparatus must be fitted up similar to the sulphuretted hydrogen generator, the bottle being replaced by a four-ounce flask; into the latter vessel about an ounce and a half of copper turnings is placed, together with a fluid ounce of strong sulphuric acid, and the cork replaced, the delivery tube being conducted into a vessel containing six ounces of distilled water. The flask is gently heated on a sand-bath, when in a short time action commences, and will continue for about twenty minutes. When the operation has finished, the delivery tube should be withdrawn from the water before taking the lamp away, otherwise the water will run up the tube into the flask, and cause an explosion.

When the greater part of the ether has evaporated, pour into the dish the six ounces of the aqueous solution of sulphurous acid made in the previous experiment, and place the evaporating basin on a saucepan of boiling water, continuing the boiling till all the water has evaporated, leaving a crystalline mass of hydrokinone.

CHAPTER VI.

PREPARATION OF SILVER NITRATE, GOLD AND PLATINUM CHLORIDE.

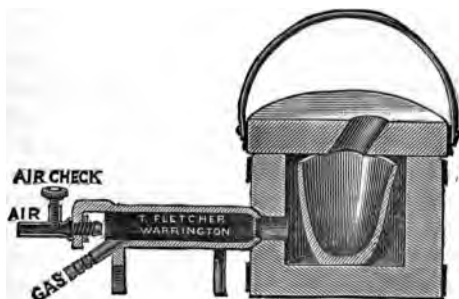
IN preparing silver nitrate, the first operation is to obtain pure silver. Of course different processes are used, according to whether the silver is in the form of an alloy or as a residue ; but the precipitation as chloride is the method which is best adapted to the requirements of the photographer.

The impure silver, whether it be silver plate or precipitated from hyposulphite solutions, is placed in a beaker, and for every ounce of the metal pour into the vessel an ounce of strong nitric acid, and warm the mixture till all the metal is dissolved. If old-fashioned plates be treated with nitric acid, very often a slight residue of gold is left undissolved, the reason being that the separation of gold from silver was not so perfect in former days as at the present time.

When the solution of the metal is complete, the liquid is diluted with an equal volume of water, and common salt is added till no further precipitate is produced ; rather more than half the weight of the original metal

is generally required to ensure the perfect precipitation of the silver chloride. After allowing the mixture to stand for a few minutes till the precipitate has settled, the top liquid containing the impurities should be carefully decanted off, and the beaker refilled with water, the operation of washing by decantation being repeated. Having obtained the silver chloride, the next operation is to reduce it to the metallic state, which may be accomplished in several ways—viz., fusing the chloride with a mixture of potassium and sodium carbonate, reducing the precipitated chloride with metallic zinc suspended in a dilute acid, or by gently fusing the chloride, and placing a piece of pure zinc in the fused mass, and, when cool, pouring dilute acid over it.

These methods are equally successful in bringing about the desired result; but it depends entirely upon the apparatus which the student happens to have at his disposal. Thus, if he possesses a good furnace, we should advise him to work with the first-named process, while if not, he must content himself with using either of the other processes.



When working by the first-named process, a good blast furnace is required, either of the form known as the

Sefström, fed with coke, or, where gas is attainable, a Fletcher's injector furnace is preferable (see fig., page 43). The dried silver chloride, mixed with rather more than half its weight of an equal mixture of potassium and sodium carbonate, and about one-fourth its weight of borax, is put into a clay crucible, fitted with a loose lid, and placed in the furnace for about twenty minutes. The crucible should be examined from time to time during the operation, and after the mixture has been in a complete fusion for five or six minutes, the liquid must be poured into a dry tile and allowed to cool down. The button of silver is best separated from the slag by treating it with hot water, thus leaving pure metallic silver ready for conversion into the nitrate.

For reducing by zinc, the silver chloride should be placed in a beaker and covered with a ten per cent. solution of sulphuric acid, about an equal weight of chip zinc being mixed with the silver compound. In a very short time the white chloride of silver nearest to the zinc will be seen to turn to a grey substance consisting of spongy metallic silver; every few minutes the mixture should be stirred, so that a fresh quantity of the chloride may come in closer contact with the zinc, and after two or three hours the whole of the chloride will be reduced. All that is necessary in order to obtain pure silver is to wash the spongy metal by decantation with three or four changes of water. The disadvantage of the process is, that a small amount of the chloride is apt to escape reduction; but if the silver compound be melted first, it forms one compact mass, and consequently does not require stirring. The silver chloride, after being thoroughly dried, is placed in a porcelain crucible, and heat applied till the whole is melted; the lamp is then taken away, and a piece of zinc placed in the

acid is poured into the crucible, and left for about half an hour till the grey mass has changed to brown spongy metallic silver. Any zinc remaining after the action is complete should be taken out, the acid liquor poured off, and the spongy silver thoroughly stirred up with water, to wash away the adhering impurities. Having obtained the pure silver, the remaining operation is very simple; the silver is placed in a beaker, and strong nitric acid poured into it, about three-quarters of a fluid ounce of the acid, sp. gr. 1.4, for every ounce of the metal is sufficient; the beaker is heated till the whole of the silver dissolves, the solution is then poured into an evaporating basin, and the excess of acid driven off by boiling. The operations of dissolving the metal and evaporating the acid solution should be conducted in the open air, as the acid fumes are very objectionable if inhaled. In order to recrystallize the salt, dissolve it in the smallest possible quantity of boiling water, and, on cooling, the solution will deposit beautiful crystals of pure silver nitrate. Of course the salt remaining in the mother liquor may be recovered by evaporation, and preserved as a less pure sample.

When preparing gold chloride from coins or jewellery, one meets with the same impurity as in making silver nitrate—viz., copper; thus it is necessary to purify the gold before converting it into a chloride. The gold is put into a beaker, and a mixture of three parts of hydrochloric and one of nitric acid (*aqua regia*) is poured into it, and heat applied till the metal is dissolved; the excess of acid is then expelled by evaporation. The impure gold chloride, when free from acid, is dissolved in *boiling water*, and a cold saturated solution of protosulphate of iron added till a dark precipitate of pure gold is no longer produced—about two ounces of the crystallised sulphate of

liquid. When cold, a ten per cent. solution of sulphuric iron being sufficient to reduce one ounce of gold chloride. The precipitate of gold must be poured on a filter and washed by pouring boiling water constantly over it till the wash-water no longer produces a precipitate with a solution of barium chloride, proving that the gold is free from the excess of sulphate of iron. The gold is redissolved in *aqua regia*, and the solution evaporated to dryness, the latter part of the operation being carried on slowly on a sand-bath, to prevent spurting. The yellow crystalline chloride of gold thus prepared should be preserved in a well-stoppered bottle or in a sealed tube, as the salt is very deliquescent.

Perchloride of platinum, or platinic chloride, a substance sometimes used for toning, is prepared in a similar manner to chloride of gold, the same precaution to expel the last traces of acid at a gentle heat being observed.

Bichloride of platinum, or platinous chloride, may be prepared by gently heating the platinic chloride; but if the temperature rises beyond a certain point, the platinous salt is reduced to the metallic state. The best method of reducing the plantinic chloride is to add a saturated solution of sulphurous acid (as described in the previous chapter) to an aqueous solution of the salt, when a yellow precipitate of platinous chloride is produced; this is washed and dried, and, if required for photographic purposes, must be converted into the double chloride of potassium and platinum, which is soluble in water.

To prepare this salt, mix twenty-seven parts of platinous chloride with eight parts of potassium chloride, dissolve in a small quantity of hot water, and evaporate to dryness; the residue being chloroplatinite of potassium, the substance used in the platinotype process.

CHAPTER VII.

ESTIMATION OF SILVER NITRATE, CHLORIDE, BROMIDE, AND IODIDE OF POTASSIUM.

IN silver estimations, a standard solution of sodium chloride and a dilute solution of *neutral* potassium chromate is required.

For preparing the standard solution, absolutely pure sodium chloride must be prepared, unless colourless rock salt can be obtained. Dissolve about three ounces of common salt in the smallest quantity of water, filter the solution, and add to it about three times its volume of pure, strong hydrochloric acid, when a white precipitate of pure sodium chloride will be formed. Filter the acid liquor, and wash the precipitate on the filter with a little dilute hydrochloric acid (1 : 4), and transfer the salt from the filter to a large porcelain crucible. Heat gently at first, and when all the moisture and acid are driven off, increase the temperature for a few minutes, so as to make certain any trace of adhering moisture is expelled. When cool, powder the salt, and preserve it in a *dry* well-stoppered bottle.

Weigh very carefully 58.5 grammes of powdered colourless rock salt, or salt prepared as above, place a small funnel in the neck of a *litre flask*, put the weighed amount of salt in the funnel, wash the salt into the flask with water by means of the wash-bottle, and fill the flask up to the graduation with distilled water. When all the salt is dissolved, pour the standard solution into a dry stoppered bottle, and label it

Standard Solution.—Sodium Chloride.

1 c. c.	=	0.585	grammes sodium chloride
„	=	.17	„ silver nitrate
„	=	.108	„ silver.

To perform an analysis of commercial silver nitrate, weigh out exactly 3.4 gramme of the sample, dissolve it in about 30 c. c. of distilled water, and make the solution up to exactly 50 c. c. by the addition of water. The object of dissolving the salt in a small quantity of water, and afterwards diluting it, instead of dissolving it at once in the 50 c. c., is that a solution of silver nitrate occupies a greater volume than the water in which it is dissolved. Pour the solution into a burette, take 10 c. c. of the standard sodium chloride by means of a pipette, and place it in a small evaporating-basin with two drops of a three-grain solution of neutral potassium chromate. Let the silver solution drip slowly from the burette into the basin, stirring its contents with a glass rod till a permanent blood red precipitate is formed, when at once turn off the tap of the burette, and note how many c. c. of the silver solution has run out.

In order to calculate the result, multiply the amount of silver nitrate which one c. c. of the standard solution of sodium chloride is equal to, by the amount of the latter

solution taken. Divide the product by the number of c. c. of silver solution run out of the burette, and multiply the quotient by the amount of water used to dissolve the sample of silver nitrate.

The calculation may seem a little difficult at first sight, but an example will make the rule more intelligible. First turn to the label on the bottle of sodium chloride solution, we see that 1 c. c. = $\cdot 17$ of silver nitrate; now $\cdot 17$ multiplied by 10 (the amount of standard solution placed in the dish) gives 1.7. We will suppose that 26 c. c. of silver solution was run out, therefore 1.7 divided by 26 equals $\cdot 0,654$; but 50 c. c. was used to dissolve the silver nitrate, therefore $\cdot 0,654$ multiplied by 50 equals 3.27, the amount of pure silver nitrate contained in 3.4 grammes of the sample analysed; or, calculated in percentage, it equals 96.2 per cent.

To determine the amount of silver nitrate in a negative bath, fill the burette with the bath solution, instead of the solution made by dissolving the sample of silver nitrate in 50 c. c. of water, and proceed exactly as in the analysis of silver nitrate. To calculate the result, multiply the number of c. c. of standard sodium chloride solution used by the amount of silver nitrate, which is equal to 1 c. c. of the standard solution, and divide the product by the number of c. c. of the bath solution run out at the burette, the quotient being the amount of silver nitrate contained in 1 c. c. of the silver bath.

For example, the burette was filled up to the top graduation with an old silver bath, 10 c. c. of standard sodium chloride solution (1 c. c. of which equals $\cdot 17$ gramme of silver nitrate) was poured in the dish, and 12 c. c. of the silver bath was required to produce a permanent red precipitate; therefore, 10 multiplied by $\cdot 17$ equals 1.7,

and 1.7 divided by 12 equals .14 grammes, the amount of silver nitrate contained in 1 c. c. of the bath solution, or about 57 grains to the ounce.

In estimating soluble chlorides, bromides, or iodides, a standard solution of silver nitrate is required. Weigh out exactly 17 grammes of silver nitrate (the triple crystallized, if dry and colourless, will answer the purpose), and transfer it to a small funnel placed in the neck of the litre flask, washing the adherent crystals into it by means of a wash-bottle, and, when the salt is dissolved, fill the flask up to the graduation with distilled water, pour the solution into a large stoppered bottle, and label it

Standard Solution.—Silver Nitrate.

1 c. c.	=	.017	gramme silver nitrate
„	=	.00,585	„ sodium chloride
„	=	.0,119	„ potassium bromide
„	=	.0,098	„ ammonium bromide
„	=	.0,166	„ potassium iodide

To analyse a sample of potassium bromide, weigh out exactly .238 grammes of the salt, dissolve it in about 20 c. c. of distilled water, and pour the solution into a small evaporating dish with two or three drops of the dilute solution of potassium chromate. Fill a burette with the standard solution of silver nitrate, and allow the solution to slowly drop out through the stop-cock into the solution of potassium bromide, and proceed with the process exactly as described above in the analysis of silver nitrate.

To calculate the result, multiply the amount of potassium bromide, which 1 c. c. of silver nitrate solution represents (see label), by the number of c. c. of standard silver solution run out of the burette, and the product is the amount of the pure salt contained in .238 grammes of the sample.

For example : $\cdot 238$ grm. of potassium bromide was taken, and $19\cdot 5$ c. c. of silver solution required to produce a permanent precipitate ; therefore, as 1 c. c. of the standard solution represents $\cdot 0,119$ grammes of potassium bromide, $\cdot 0,119$ multiplied by $19\cdot 5$ equals $\cdot 232$ grammes of pure salt contained in $\cdot 238$ grammes of the sample under examination, or $97\cdot 5$ per cent.

For analysing ammonium bromide by this method, $\cdot 196$ gramme should be taken ; while for potassium iodide as much as $\cdot 332$ grammes are required. The amount of soluble bromide contained in a washed or unwashed gelatine emulsion can easily be estimated by this process.

For example : 50 c.c. of unwashed emulsion was poured into an evaporating basin, with about an equal volume of distilled water, and two or three drops of a dilute solution of potassium chromate. Standard silver solution was run in till a permanent red precipitate was formed, 5 c. c. being required ; therefore, as 1 c. c. of silver solution represents $\cdot 0,098$ gramme of ammonium bromide (the soluble bromide used in the preparation of the emulsion), $\cdot 0,098$ multiplied by 5 equals $\cdot 049$ gramme, the amount of excess of soluble bromide contained in 50 c. c. of the emulsion.

CHAPTER VIII.

ESTIMATION OF ACIDS, AMMONIA, AND PROTOSULPHATE OF IRON.

FOR estimating acid and alkaline solutions, a standard solution of both sodium carbonate and sulphuric acid is required.

To prepare the first-named solution, place about two ounces of pure dried sodium carbonate in a porcelain crucible and heat it over a Bunsen burner for about ten minutes, to drive off any trace of adherent moisture. When cold, powder the substance in a dry mortar, and transfer the powdered salt to a dry, well-stoppered bottle. Weigh out exactly 53 grams of the above dried salt, place it in a litre flask with a small quantity of water, and, when dissolved, dilute with distilled water to exactly a litre. The solution must be preserved in a stoppered bottle, and should be labelled—

Standard Solution.—Sodium Carbonate.

1 c.c.	=	·053	grams sodium carbonate
„	=	·017	„ ammonia
„	=	·049	„ sulphuric acid
„	=	·0365	„ hydrochloric acid
„	=	·063	„ nitric acid

To prepare the acid solution, place 28 c.c. of pure strong sulphuric acid in a litre flask containing about 300 c.c. of distilled water, and, when the solution is cool, dilute it to a litre. After preparing the solution it is necessary to ascertain the exact strength of it by means of the standard solution of sodium carbonate, for it is impossible to weigh out the exact amount of acids, as it varies in strength. Fill a burette with the solution of sulphuric acid to be tested, place in a small flask 10 c.c. of standard sodium carbonate solution with about 100 c.c. of distilled water, and a sufficient quantity of solution of litmus to give the liquid a light blue colour. Allow the acid to slowly drip out of the burette into the flask until its contents has acquired a red tint; then boil the solution till the blue colour returns, and again run the acid out of the burette as before. This operation must be repeated till a permanent red tint remains even after boiling for several minutes.

The red tint first formed is produced by the carbonic acid set free in the decomposition of sodium carbonate by the sulphuric acid, but on boiling, the gas is insoluble, and consequently escapes, allowing the remaining undecomposed sodium carbonate to colour the litmus blue. When sufficient acid is added to produce a permanent red tint, the whole of the sodium carbonate is decomposed, and the slight excess of sulphuric acid preserves the red tint, although, on boiling, all the carbonic acid gas is driven off. It will be noticed that the red colour produced by the carbonic acid is of a light claret tint, whilst with sulphuric acid an onion red colour is produced. An experienced analyst can work without boiling the solution by running in the acid till the claret tint first produced gives way to the onion red colour; but as it is rather difficult to determine when the exact point is reached, we

should certainly not advise the student to perform the operation without boiling.

In order to calculate the strength of the acid solution, multiply the amount of acid which is equal to 1 c.c. of the standard sodium carbonate by the number of c.c. of standard sodium carbonate used, and divide the product by the number of c.c. of sulphuric acid solution run out of the burette; the quotient is the amount of acid contained in 1 c.c. of the solution.

For example: 10 c.c. of standard sodium carbonate was used (1 c.c. = .049 sulphuric acid), and 9 c.c. of sulphuric acid was required to produce the permanent red colour; therefore 10 multiplied by .049 equals .49, and .49 divided by 9 equals .0544, the amount of sulphuric contained in 1 c.c. of the solution. The amount of ammonia equal to 1 c.c. of the sulphuric acid can be calculated in the same way, substituting .017 (the amount of ammonia which corresponds to 1 c.c. of the sodium carbonate solution) for .049 in the above example. The sulphuric acid should be labelled—

Standard Solution.—Sulphuric Acid.

1 c.c. = x sulphuric acid

„ = y ammonia

Of course x and y must be determined for every solution made up, but in the above example it equals .0544, and y equals .019. In order to determine the amount of ammonia in a solution, fill a burette with the standard solution of sulphuric acid, and place 10 c.c. of the solution of ammonia in a flask with a little litmus solution, and run the acid from the burette into the ammonia, shaking the flask gently, till a red colour is produced. In this process the solution is not boiled, because there is no carbonic acid

to interfere with the reaction, and also heating the solution would drive off the ammonia.

To calculate the result, multiply the number of c.c. of standard acid solution by the amount of ammonia which is equal to 1 c.c. of the standard acid, and divide the product by the number of c.c. of solution of ammonia used in the analysis; the quotient is the amount of ammonia contained in 1 c.c. of the solution tested.

For example: 10 c.c. of an ammonia solution, used for pyrogallie development, was taken, and 20 c.c. of standard acid (1 c.c.=.019 grm. ammonia) required to produce a red colour; therefore .019 multiplied by 20 equals .38, and .38 divided by 10 equals .038 grms., the amount of ammonia contained in 1 c.c. of the ammoniacal solution tested, which is equivalent to 3.8 per cent. Strong ammonia, sp. gr. 880, contains 33 per cent. of ammonia, therefore the ammoniacal solution contains rather more than 11 per cent. of strong ammonia.

There are several methods for estimating the amount of ferrous sulphate contained in commercial protosulphate of iron, but the bichromate process is the most accurate.

It is necessary to have a standard solution of potassium bichromate, and a dilute solution of ferricyanide of potassium. To prepare the first-named solution, place about 12 grms. of recrystallized potassium bichromate in a porcelain crucible, and heat gently to fusion. When cold, powder the salt, and preserve it in a stoppered bottle. Weigh out exactly 9.834 grm. of the above dried salt, dissolve it in a small quantity of water in a litre flask, and fill up to the litre graduation with distilled water. Transfer the solution to a stoppered bottle and label thus—

Standard Solution.—Potassium Bichromate.

1 c.c. = .009834 grm. potassium bichromate

1 c.c. = .0488 grm. crystal ferrous sulphate.

To determine the amount of ferrous sulphate in a commercial sample, weigh out exactly 2.44 grms. of the salt, dissolve it in a beaker in about 300 c.c. of boiled cold distilled water, and add to the solution about 10 c.c. of dilute solution of sulphuric acid (1 : 4). Fill a burette with the standard solution of potassium bichromate, sprinkle over a white plate a one-grain solution of potassium ferricyanide (red prussiate of potash) by means of a glass rod. Run the bichromate solution out of burette into the solution of ferrous sulphate, testing the solution from time to time by taking a drop out with a glass rod, and touching one of the drops of ferricyanide on the plate; at first, a blue precipitate will be produced, but when sufficient bichromate has been run in, instead of a blue precipitate being produced, a brown colour will form on touching the ferricyanide. To calculate the result, all that is necessary is to multiply the number of c.c. run of the burette by .0488 (the amount of ferrous sulphate which is equivalent to 1 c.c. of bichromate solution); the product represents the amount of pure ferrous sulphate contained in 2.44 grm. of the sample.

CHAPTER IX.

ESTIMATION OF HYPOSULPHITE OF SODA, OXALIC ACID, OXALATE OF POTASH, AND CHLORIDE OF GOLD.

HYPOSULPHITE of soda is frequently contaminated with sulphate of sodium and other salts, which are quite incapable of acting as fixing agents; it is therefore very important that the photographer should know how to estimate the amount of hyposulphite—or thiosulphate, as it now termed—contained in the commercial salt.

A standard solution of iodine and a solution of starch is required. To prepare re-sublimed iodine for the first-named solution, place in a small evaporating-basin about 15 grms. of pure iodine and 3 grms. of potassium iodide, cover the vessel with a rather larger basin full of cold water, and heat the lower basin gently over a sand-bath, when the iodine will vaporise and condense in grey crystals on the outside of the upper basin. The crystals should be occasionally scraped off with a glass rod, and preserved in a stoppered bottle, the water in the upper basin being changed at the same time.

Weigh out exactly 12·7 grms. of the above re-sublimed iodine, about 18 grms. of pure white potassium iodide, and

dissolve in exactly a litre of water in the usual way. The solution must be kept in small bottles filled up to the neck, and always in a dark place, otherwise it soon loses its strength. The bottles should be labelled thus:—

Standard Solution.—Iodine.

1 c.c. = .0127 grm. iodine.

„ = .0248 „ hyposulphite of soda.

The starch solution is made by pouring about 50 c.c. of boiling water on to about 5 grms. of pure white starch made into a paste with a little water. If 10 c.c. of alcohol be added to the solution, it will keep for about a month. In order to perform an estimation, weigh out exactly .496 grm. of the sample of hyposulphite of soda, dissolve it in a small flask in about 200 c.c. of water, and add a few drops of the starch solution. Fill a burette with the standard solution of iodine, and allow the solution to slowly run into the flask containing the hyposulphite and starch, till a permanent blue colour is produced, showing that all the hyposulphite has been decomposed by the iodine, and the slight excess colours the starch blue.

To calculate the result, multiply the amount of hyposulphite (which is equivalent to 1 c.c. of the iodine solution) by the number of c.c. run out of the burette; the product is the amount of pure hyposulphite contained in .496 grm. of the salt tested. Thus, supposing 19.5 c.c. of iodine solution was run out of the burette, .0248 multiplied by 19.5 equals .4836, the amount contained in .496 grm. of the sample, which is equivalent to 97.6 per cent.

For estimating gold chloride, oxalic acid, and oxalate of potash, a standard solution both of oxalic acid and potassium permanganate is required.

For the first solution, pure re-crystallized oxalic acid

must be prepared, and thoroughly dried in several pieces of bibulous paper, taking care to use the acid as soon as possible, otherwise it will slowly effloresce. Weigh out exactly 63 grms. of the pure acid, and dissolve it in the usual way in a litre of water. The solution will keep well and should be labelled thus :—

Standard Solution.—Oxalic Acid.

1 c.c. =	·063	gram.	oxalic acid.
„ =	·092	„	neut. potassium oxalate
„ =	·0316	„	potassium permanganate.
„ =	·101	„	gold chloride.

To prepare the second standard solution, weigh out exactly 31·6 gram. of pure potassium permanganate, and dissolve it in the usual way in a litre of distilled water. If the salt be perfectly pure, 10 c.c. of the solution should be exactly equal to 10 c.c. of the standard solution of oxalic acid; but as the solution is very liable to be somewhat weaker from the presence of impurities in the permanganate of potassium, it is necessary to standardise the solution before using it. Fill a burette with the permanganate solution, place exactly 10 c.c. of standard oxalic acid in a flask with 2 or 3 c.c. of dilute sulphuric acid (1:4) and about 500 c.c. of distilled water. Warm the contents of the flask to about 140° F. (60° C.), and run the permanganate from the burette into the flask, till a permanent pink colour is produced in the solution, even when heated till nearly boiling. If exactly 10 c.c. is required, the solution should be labelled—

Standard Solution.—Potassium Permanganate.

1 c.c. =	·0316	gram	potassium permanganate
„ =	·092	„	neutral potassium oxalate
„ =	·063	„	oxalic acid

If more than 10 c.c. of permanganate solution be required, in standardising, the above numbers must be multiplied by 10, and the product divided by the number of c.c. of permanganate required to produce the pink colour. Thus, supposing 10.1 c.c. were used in the above experiment, in order to calculate the amount of potassium permanganate really contained in the solution, we first note that in the above label 1 c.c. = 0.316, therefore 0.316 multiplied by 10 equals 3.16, and 3.16 divided by 10.1 equals 0.31179, the exact amount of permanganate contained in 1 c.c.

In order to analyse commercial samples of oxalic acid, weigh out 1.26 grm. of the substance, dissolve it in about 300 c.c. of water with 2 c.c. of dilute sulphuric acid, and heat to about 140° F. Run the above permanganate standard solution in the usual way out of a burette into the solution till a permanent pink colour is produced.

To calculate the result, multiply the amount of oxalic acid which is equal to 1 c.c. of permanganate, by the number of c.c. run out of the burette; the quotient is the amount of pure oxalic acid contained in the weight of the substance originally taken. Thus, for example, 1.26 grms. of commercial oxalic acid was used, and 19.5 c.c. of permanganate (same strength as the above label) was run out of the burette; therefore 19.5 multiplied by 0.063 equals 1.2285 grms, the amount contained in 1.26, or 97.6 per cent. To analyse oxalate of potassium by this process, dissolve 1.84 grms. in 300 c.c. of water, add 5 c.c. of dilute sulphuric acid, and proceed as in the above method.

For example: 1.84 grms. was used, and 19.8 c.c. of standard solution of permanganate required to produce the pink colour, therefore 19.8 multiplied by 0.092 (the amount of oxalate of potassium which is equivalent to 1 c.c. of the standard solution) equals 1.8216 grms., the weight of

pure potassium oxalate contained in 1.84 grms. of the substance. If the sample shows an acid reaction, the percentage may, on analysis by the above process, appear to be over a hundred, from the presence of an excess of oxalic acid in the salt.

To analyze chloride of gold, weigh out 1.01 grm. of the sample, dissolve it in about 10 c.c. of water, add 15 c.c. of standard solution of oxalic acid, and add sufficient distilled water to make the volume up to exactly 300 c.c. Keep the solution in a warm place for about twenty-four hours, when the chloride of gold will be reduced to the metallic state, forming a deposit at the bottom of the vessel. When the reduction is completed, transfer 100 c.c. of the solution by a pipette to a flask containing about 300 c.c. of distilled water with 2 or 3 c.c. of dilute sulphuric acid, and run in from a burette standard solution of permanganate, as in the above process for estimating oxalic acid.

To calculate the result, multiply the number of c.c., run out of the burette by 3, and subtract the product from the number of c.c. of standard solution of oxalic acid, provided 1 c.c. of permanganate is exactly equal to 1 c.c. of the oxalic acid (otherwise, of course an allowance must be made for the difference); the remainder, when multiplied by .101, equals the amount of pure gold chloride contained in 1.01 grm. of the sample.

CHAPTER X.

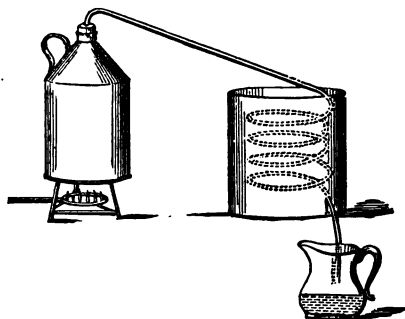
COLLECTING AND WORKING-UP RESIDUES.

As a good deal of interest has been taken in the treatment of residues of late, we make no apology for concluding this series of lessons by describing the processes proved to work best in practice. We shall consider the subject under five headings, viz., alcohol, gold, oxalate, platinum, and silver.

Alcohol.—Now that this liquid is being used so extensively for precipitating gelatine emulsion, hardening and facilitating the drying of gelatine plates, it is very important that photographers should know how to recover the alcohol for future use. The desired result may be obtained either by treating the dilute alcohol with dry potassium carbonate, or by distilling the liquid over quick-lime. In the first process, the potassium carbonate forms with the water a saturated solution which will not mix with the alcohol, thus allowing it to separate, and from its low specific gravity rises to form an upper liquid. The alcohol is drawn off by a syphon, and the solution of potassium carbonate evaporated down ready for future separation.

The objection to this process is that it does not free the alcohol from all the water, and is very liable to leave certain impurities still dissolved. Although the alcohol might be used with impunity for precipitating gelatine emulsion, the liquid would not be sufficiently pure for a great many photographic processes ; it is therefore preferable to purify all alcoholic residues by distilling over lime.

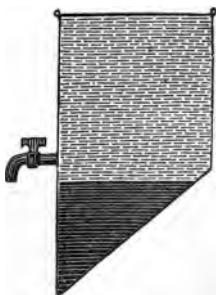
For alcoholic distillations, an apparatus consisting of a tin oil-can of suitable size, fitted with a perforated cork, is required. A piece of lead pipe half-an-inch in diameter, and about six feet long, one end of which is inserted in the perforated cork, while the other end is bent into a spiral, serves to condense the liquid. The spiral tubing is placed in a small tub or barrel having a hole just large enough to admit the end of the tubing (see figure).



The alcohol residue mixed with an equal weight of fresh quick-lime is placed in the tin can on a sand-bath or a saucepan of water, and heat applied, when the pure alcohol vaporises and condenses in the spiral tubing. The vessel enclosing the spiral must always be kept full of cold water, the warm water being occasionally drawn off from the

surface, while cold water is added down a tube at the bottom. Alcohol purified in this way contains about five per cent. of water, and is quite strong enough for all photographic purposes, except for the manufacture of collodion.

Gold.—Most photographers neglect the gold contained in old toning baths, on account of the small amount contained therein, and no doubt in small establishments it is hardly worth troubling about, but in large establishments, where a great deal of silver printing is done, the collection of residues should always be attended to. A large barrel, tub, or wedge-shaped tank (see figure) should be set apart,



Section of Residue Tank.

wherein all used toning baths are collected, and when the vessel is full, a solution should be added, containing about thirty grains of protosulphate of iron for every gallon of the residue contained in the tank. After allowing the liquid to stand for about twelve hours, the supernatant liquor must be drawn off by a stopcock or a syphon, leaving the residue of metallic gold, together with waste liquor to the depth of three or four inches. The remaining liquor and precipitated gold should be thrown on a filter

of bibulous paper, washed by pouring hot water over it, and, when dry, the gold is ready for conversion into chloride in the manner previously described.

Potassium Oxalate.—The ferrous oxalate developer, when once used, is generally thrown away; yet how often we hear photographers cry out at its expense; but if attention is given to re-converting the used solution into potassium oxalate, the developer will be far cheaper than any other. Either caustic potash or potassium carbonate will decompose the oxalate solution, but we prefer to use the latter compound.

The solution to be acted upon should be placed in a large beaker, and sufficient quantity of a saturated solution of potassium carbonate added till no further precipitate of carbonate of iron is produced; the solution must then be filtered through bibulous paper, and should appear perfectly colourless. If the solution is still tinted brown, it shows that the whole of the iron has not been precipitated, and that the addition of potassium carbonate and the process of filtering must be repeated.

The solution of potassium oxalate thus prepared contains a certain amount of potassium carbonate, therefore a saturated solution of oxalic acid must be added to decompose the potassium carbonate, the exact point of neutrality being found by testing the solution with litmus paper. The solution should finally be evaporated down till the salt begins to crystallize, and allowed to cool; the mother liquor can be poured off ready for use, and the crystals dissolved in sufficient water to prepare a "saturated solution."

Platinum.—If only workers of the platinotype process knew what a large quantity of platinum salt is wasted when they throw a used developer into the sink, perhaps

they would be more careful to collect platinum residues. In the first place, it must be remembered that the prepared paper is coated with a solution containing sixty grains of the platinum salt to the ounce, and that only about one-tenth of the platinum is actually deposited on the print, while about three-fourths of the salt is dissolved, and remains in the developer. It is therefore evident that in order to obtain the greater part of the waste platinum, all that is necessary is to treat the developer with a reducing agent, such as is used for obtaining gold from its solution. The following is the method which has proved most successful in our experience. Place the used developer in a large beaker, and heat the solution over a sand-bath till nearly boiling, then add to the solution one-fourth its volume of a saturated solution of protosulphate of iron; a black precipitate will be immediately produced, consisting of pure metallic platinum. The supernatant liquid, consisting of ferrous oxalate, is carefully poured off into the oxalate residues, and the precipitated platinum, after being washed by decantation, should be either converted into chloride, or sold to a refiner.

Silver.—This element is present both in the wash-water of silver prints, and the fixing solutions used for negatives and prints. In order to obtain the silver from the wash-water, the solution must be collected in a vessel similar to that used for gold solutions, and containing two or three handfuls of common salt. When the collecting tub is full, the supernatant liquor should be poured off, leaving at the bottom the precipitated chloride of silver, which must be dried, and either sold to a refiner, or mixed with an equal weight of dried sodium carbonate and fused in a furnace, as described in the lesson on the preparation of silver *nitrate*.

To obtain the silver from hyposulphite fixing baths, the solution should be collected in the usual way, and precipitated by means of sulphide of ammonium. It is impossible to give any definite quantity to insure the precipitation of the silver, but 3 per cent. of the alkaline sulphide should be added to the ordinary fixing bath used for gelatine plates, while 1 per cent. of the precipitant will suffice for solutions used for fixing silver prints.

To obtain metallic silver, the precipitated silver sulphide obtained as above, must be dried, and mixed with an equal weight of a mixture of potassium nitrate and sodium carbonate, and fused in a blast furnace.

ENGLISH WEIGHTS AND MEASURES.

APOTHECARIES' WEIGHT.

FLUID.

60 minims = 1 fluid dram.

8 drams = 1 ounce.

20 ounces = 1 pint.

SOLID MEASURE.

20 grains = 1 scruple = 20 grains.

3 scruples = 1 dram = 60 „

8 drams = 1 ounce = 480 „

12 ounces = 1 pound

The above weights are used by photographers. Chemicals are sold by—

AVOIRDUPOIS WEIGHT.

$27\frac{1}{3}$ grains = 1 dram = $27\frac{1}{3}$ grains.

16 drams = 1 ounce = $437\frac{1}{2}$ „

16 ounces = 1 pound = 7000 „

FRENCH WEIGHTS AND MEASURES.*

The unit of liquid measures is a cubic centimetre, or “c. c.”, which measures 16·896 minims, and weighs 15·4 grains, or 1 gramme—the unit of solid measures.

1 cubic centimetre = 17 minims (nearly).

$3\frac{1}{2}$ „ „ = 1 dram.

$28\frac{2}{5}$ „ „ = 1 ounce.

100 „ „ = 3 ounces, 4 drams, 9 minims.

1000 „ „ } = 35 ounces, 1 dram, 36 minims.
or 1 litre

As a gramme is equal to 15·4323 grains, in order to convert grammes into grains, multiply the former by $15\frac{1}{2}$.

* The French system of weights and measures has been adopted throughout the chapters on quantitative analysis.

LIST OF CHEMICALS WITH OLD OR COMMERCIAL TERMS.

Old or Commercial.	Modern.	Symbol.
Pyroligneous Acid ...	Acetic Acid ...	$C_2H_3O_2$...
Pyrogallal Acid ...	Pyrogallol ...	$C_6H_3O_3$...
Muriatic Acid, or Spirits of Salt	Hydrochloric Acid ...	HCl ...
Aquafortis ...	Nitric Acid ...	HNO_3 ...
Oil of Vitriol ...	Sulphuric Acid ...	H_2SO_4 ...
Spirits of Wine ...	Ethylic Alcohol ...	C_2H_5O ...
Wood Spirit ...	Methylic Alcohol...	CH_3O ...
Hartshorn ...	Ammonia ...	NH_3 ...
Muriate of Ammonia*	Ammonium Chloride	NH_4Cl ...
Blue Vitriol ...	Cupric Sulphate ...	$CuSO_4 \cdot 5H_2O$...
Sulphuric Ether ...	Ethylic Ether ...	C_2H_5O ...
Perchloride of Iron ...	Ferric Chloride ...	Fe_2Cl_6 ...
Copperas, Green Vitriol, or Protosulphate of Iron	Ferrous Sulphate...	$FeSO_4 \cdot 7H_2O$...
Corrosive Sublimate, or Bichloride of Mercury	Murcuric Chloride	$HgCl_2$...
Bichromate of Potash* ...	Potassium Bichromate	$K_2Cr_2O_7$...
Yellow Prussiate of Potash*	Potassium Ferricyanide ...	$K_3Fe(CN)_6$...
Red Prussiate of Potash*	Potassium Ferricyanide ...	$K_3Fe(CN)_6$...
Soluble Gun-cotton ...	Pyroxyline or Nitro-cellulose
Lunar Caustic ...	Argentite or Silver Nitrate	$AgNO_3$...
Common Salt ...	Sodium Chloride ...	NaCl ...
Hyposulphite of Soda*	Sodium Thiosulphate	$Na_2S_2O_3$...
Tannin ..	Tannic Acid ...	$C_{27}H_{32}O_{17}$...

* Potassium, sodium, and ammonium compounds were originally considered salts of potash, soda, and ammonia.

TABLE OF ELEMENTS

PRESENT IN SUBSTANCES USED IN PHOTOGRAPHY.

Element.			Symbol.			Weight.
Aluminium	Al ⁱⁱⁱ *	27·5
Barium	Ba ⁱⁱ	137
Bromine	Br ⁱ	80
Cadmium	Cd ⁱⁱ	112
Calcium	Ca ⁱⁱ	40
Carbon	C ^{iv}	12
Chlorine	Cl ⁱ	35·5
Chromium...	Cr ⁱⁱⁱ or Cr ^{vi}	52·5
Copper	Cu ⁱ or Cu ⁱⁱ	63·5
Fluorine	F ⁱ	19
Gold	Au ⁱⁱⁱ	196·6
Hydrogen	H ⁱ	1
Iodine	I ⁱ	127
Iridium	Ir ^{iv}	197·1
Iron	Fe ⁱⁱ or Fe ⁱⁱⁱ	56
Lead	Pb ⁱⁱ	207
Magnesium	Mg ⁱⁱ	24·3
Mercury	Hg ⁱ or Hg ⁱⁱ	200
Nitrogen	N ⁱⁱⁱ or N ^v	14
Oxygen	O ⁱⁱ	16
Palladium...	Pd ⁱⁱ or Pd ^{iv}	106·5
Phosphorus	P ⁱⁱⁱ or P ^v	31
Platinum	Pt ⁱⁱ or Pt ^{iv}	197·1
Potassium...	K ⁱ	39·1
Selenium	Se ⁱⁱ	79·5
Silicon	Si ^{iv}	28
Silver	Ag ⁱ	108
Sodium	Na ⁱ	23
Sulphur	S ⁱⁱ	32
Tin	Sn ⁱⁱ or Sn ^{iv}	118
Uranium	U ⁱⁱ or U ⁱⁱⁱ	120
Zinc	Zn ⁱⁱ	65

* The index attached to each symbol represents its atomicity, or the number of atoms of hydrogen, or other monatomic element, for which the atomic weight of the element is exchangeable in chemical combinations.

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